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NICOTINE INSECTICIDES

PART IV--PRELIMINARY TOXICITY TESTS WITH NICOTINIUM SALTS

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This is the fourth of a series of investigations on nicotine insecticides conducted by this Bureau in cooperation with the Bureau of Agricultural and Industrial Chemistry. Part I of this series (E-646 issued in 1945) reported a study of complex salts containing nicotine, usually combined with a metal. Part II (E-709 issued in 1946) described tests with a large number of materials to find activators for nicotine. Part III (E-720 issued in 1947) is a study of the effect of various carriers on the toxicity of nicotine sulfate. The present study is of the insecticidal properties of 48 nicotinium salts and reports the preliminary toxicity tests with these salts in an attempt to correlate chemical composition with toxicity to insects.

Of the numerous derivatives of nicotine prepared and tested as insecticides, the nicotinium salts have received comparatively little attention. The few published insecticide tests on compounds of this type have indicated little if any superiority to nicotine or to the nicotine compounds when tested simultaneously. For example, Swingle and Cooper (7) found that dimethyl nicotinium sulfate in combination with bentonite was relatively ineffective against the imported cabbageworm ((Ascia) Pieris rapae (L.)), the diamondback moth (Plutella maculipennis (Curt.)), the greenhouse leaf tier (Phylctaenia rubigalis (Guen)), the southern armyworm (Prodenia eridania (Cram.)), and the green cutworm ((Lycophotia) Anicla infecta (Ochs.)). Hansberry and Norton (2) reported that

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dodecyl nicotinium bromide, didodecyl nicotinium dibromide, dodecyl nicotinium iodide, and didodecyl nicotinium diiodide were inferior to nicotine alkaloid in toxicity to Aphis rumicis L. The studies of Austin, Jary, and Martin (1) indicated that the Tinocine D (a long-chain nicotinium bromide) possessed good surface-active properties and approximated nicotine in toxicity when compared on an equimolar basis against the hop aphid (Phorodon humuli (Schr.)). Dodecyl nicotinium bromide, didodecyl nicotinium dibromide, and octadecyl nicotinium bromide have been patented as insecticides by Oadeshott (4, 5) in Great Britain and in this country, but no insecticide data are disclosed in the patents.

The present study of the insecticidal properties of 48 nicotinium salts was undertaken in an attempt to correlate chemical composition with toxicity to insects, and to ascertain, if possible, the most promising nicotinium cations and anions for further concentrated efforts. In view of the fungicidal activity of nicotinium salts reported by Howard, Keil, Weil, and Woodward (3) and in further consideration of the data herein reported, it appears probable that certain derivatives of this class may have both insecticidal and fungicidal properties. This paper deals only with preliminary tests in which an attempt was made to obtain some indication of possible promising compounds in this series.

Materials

The nicotinium halides listed in tables 1 and 2 were prepared by reaction of the corresponding alkyl or aralkyl halides with nicotine according to the procedure of von Walther and Weinhausen (8). The monoalkyl and monoaralkyl nicotinium halides resulted from chemical combination of the appropriate organic halide with nicotine in equimolecular proportions. In the cases of the monoaralkyl nicotinium halides it was assumed that the organic halides had reacted predominately with the nitrogen of the N-methylpyrrolidine nucleus of nicotine because it is more basic than the pyridyl nitrogen. The dialkyl and diaralkyl nicotinium dihalides were prepared by reacting the corresponding organic halides with nicotine in a molecular ratio of 2:1. The nicotinium p-toluenesulfonates were prepared by essentially the same procedure as was employed for the nicotinium halides.

The salts containing anions other than halides or p-toluenesulfonates were prepared by the metathetical reaction of a nicotinium halide with the sodium or potassium salt of the appropriate anion.

Comparisons of the toxicities of the nicotinium salts with nicotine or nicotine sulfate were made on an equimolar basis in both sprays and dust applications. In tests with dusts the quantity of nicotinium salt equivalent to 5 percent of nicotine was mixed with pyrophyllite.

The following insects were used in these tests: First and fourth instars of the southern armyworm (Prodenia eridania (Cram.)); fourth instars of the melonworm (Diaphania hyalinata (L.)), the southern beet webworm (Pachyzancla bipunctalis (F.)), and the bean leaf roller (Urbanus proteus (L.)); adults of the three-striped blister beetle (Epicauta lemniscata (F.)), spider mites (Tetranychus spp.), and an aphid, Macrosiphum ambrosiae (Thos.).

Methods and Procedure

The procedure used in testing the nicotinium salts was similar to that described by Swingle (6) and reported in Part I of this series. In tests against the melonworm sprays or dusts were applied to pumpkin leaves, and sections of these leaves were then fed to fourth instars in petri dishes. Fourth instars of the southern armyworm and the southern beet webworm, and adults of the blister beetle were exposed in a similar manner to dusted or sprayed pigweed leaves. First instars of the southern armyworm were allowed to feed on dusted or sprayed sections of collard leaves in cloth-covered vials. The bean leaf roller was allowed to feed on sprayed sections of bean leaves in petri dishes. The host plant for the spider mites was celery and for the aphids, wild lettuce. All toxicant applications were in spray form in tests against the spider mite, and Macrosiphum ambrosiae.

Although the procedures used afford an opportunity for fumigating action, as well as stomach-poison and contact action, it is believed that the nicotinium salts are ineffective as fumigants since they are essentially nonvolatile.

The approximate numbers of insects employed in the tests were as follows: Leaf-feeding larvae and adult blister beetles, 20-30; spider mites, 75-150; Macrosiphum ambrosiae, 40-150.

In spray tests the mortality counts on the leaf-feeding larvae and the blister beetles were generally made 2 and 4 days after the toxicant applications, whereas in the dust tests they were made 2 or 3 days after. Departures from this procedure were occasionally made in the case of unusually high or low mortalities, or heavy feeding. Mortality counts on the spider mites and the aphids were made 2 days after the applications.

Discussion of Results

It was impossible to test all the nicotinium compounds against all seven species of insects listed above, since many of them were available for only part of the testing period. Only the melonworm and the southern armyworm were employed throughout the tests; consequently this discussion of relative effectiveness is based largely on the tests against these two insects. Test data on the compounds showing a higher toxicity than that shown by the nicotine or nicotine sulfate standard on the same

day to either or both of these insects are listed in table 1. This table also gives data on all insects against which the compounds were tested.

Compounds that were relatively nontoxic to all the insects against which they were tested are listed in table 2. Except where indicated otherwise, the compound was less toxic than the stipulated standard.

Dimethyl nicotinium diiodide and methyl nicotinium iodide gave higher mortalities of the insects against which they were tested than were obtained by the use of the standard. Dodecyl nicotinium p-toluenesulfonate was more toxic than the nicotine standard to the melonworm and to the first-instar southern armyworm, but less toxic than DDT to the fourth-instar southern armyworm or than lead arsenate to the bean leaf roller. The other compounds listed in table 1 were relatively nontoxic to the southern armyworm, whereas all the compounds were more toxic than nicotine sulfate or nicotine to the melonworm.

It appears that the dodecyl cation is more toxic than the other cations, since 8 of the 10 dodecyl compounds tested are found in table 1. The methyl cation group seems to be second best, since 2 of the 3 materials containing this cation are found in table 1. Among the anions, the only iodide, diiodide, and propionate tested appear in table 1, whereas the dibromide and oleate ions appear once in each table. The number of compounds and the number of tests with each compound make these comparisons indicative rather than conclusive.

Summary

The toxicity of 48 nicotinium salts to the melonworm (Diaphania hyalinata (L.)), the southern armyworm (Prodenia eridania (Cram.)), spider mites (Tetranychus spp.), and to certain other insects was investigated in a limited number of preliminary tests.

Methyl nicotinium iodide, dimethyl nicotinium diiodide, and dodecyl nicotinium p-toluenesulfonate were more toxic to insects used than nicotine sulfate, or nicotine, when tested on the basis of equal amounts of nicotine. In addition, 13 other compounds were found to be more toxic to the melonworm than the nicotine, or nicotine sulfate standard.

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Table 1.--Test data on the most promising nicotine salts selected on the basis of toxicity to larvae of the melonworm and the southern armyworm

Compound and insect <u>2/</u>	: Extent : : of : : Feeding :	Deposit <u>1/</u>		: Standard <u>3/</u> :	Mortality	
		Compound	:	Compound	Percent	Days
			:		Percent	Days
Benzyl nicotine thiocyanate:						
Melonworm	Normal	120		125	4	3
	Moderate	0.15		0.15	53	4
	Trace	100		105	100	3
Southern armyworm	Moderate	0.15		0.15	31	4
	-do-	0.075		0.075	14	4
Didodecyl nicotine dibromide:						
Melonworm	-do-	0.2		0.2	100	4
Southern armyworm	-do-	105		100	0	3
	-do-	0.2		0.2	4	3
Didodecyl nicotine dichloride:						
Melonworm	-do-	0.15		0.15	73	4
Southern armyworm	Normal	0.15		0.15	4	4
	-do-	0.075		0.075	7	4
Dimethyl nicotine diiodide:						
Melonworm	Moderate	0.2		0.2	88	4
Southern armyworm	-do-	95		100	94	3
	-do-	0.2		0.2	96	3
Dodecyl nicotine bromide:						
Melonworm	-do-	130		125	100	3
	-do-	0.15		0.15	100	3
Southern armyworm	Normal	100		100	0	3
	-do-	0.15		0.15	15	4
	Moderate	0.075		0.075	11	4

Table 1.--Continued

Compound and insect <u>2/</u>	: Extent : : of : : Feeding :	Deposit <u>1/</u>		: Standard <u>3/</u> :	Mortality	
		Compound :	:	Compound :	Compound :	Standard :
					Percent Days	Percent Days
Dodecyl nicotinium chloride:						
Melonworm	Moderate	0.3		0.3	70	41
Southern armyworm	Trace	0.3		0.3	4	96
	Moderate	0.15		0.15	7	62
Dodecyl nicotinium oleate:						
Melonworm	-do-	0.2		0.2	95	43
Southern armyworm	-do-	100		100	0	66
	-do-	0.2		0.2	21	76
Dodecyl nicotinium propionate:						
Melonworm	-do-	0.2		0.2	100	43
Southern armyworm	-do-	95		100	7	66
	-do-	0.2		0.2	17	76
Dodecyl nicotinium thiocyanate:						
Melonworm	Trace	130		125	95	50
Southern armyworm	Moderate	0.15		0.15	100	59
	Normal	100		100	0	66
	-do-	0.15		0.15	19	100
	Moderate	0.075		0.075	5	100
Dodecyl nicotinium p-toluene-sulfonate:						
Melonworm	-do-	0.1		0.1 (N)	90	23
Southern armyworm	-do-	0.1		0.1 (N)	13	7
I-4	Normal	0.1		0.1 (DDT)	29	63
Bean leaf roller	Moderate	0.1		0.25 (LA)	29	100

Table 1.--Continued

Compound and insect ^{2/}	: Extent : : of : : Feeding :	Deposit ^{1/}		Mortality	
		Compound :	Standard ^{3/} :	Compound :	Standard
		Percent	Days	Percent	Days
Methyl nicotinium iodide:					
Melonworm	Moderate	0.2	0.2	95	43
Southern armyworm	-do-	100	100	90	66
	-do-	0.2	0.2	96	76
Octyl nicotinium thiocyanate:					
Melonworm	-do-	125	125	74	50
	-do-	0.15	0.15	44	59
Southern armyworm	Normal	100	100	0	66
	Moderate	0.15	0.15	52	100
	-do-	0.075	0.075	88	100

^{1/} All numbers greater than 1 are dust applications expressed in micrograms per square centimeter. Numbers less than 1 are spray applications expressed in percent of contained nicotine in toxicant.

^{2/} Melonworm and bean leaf roller specimens were fourth instars, those of the armyworm first instars except where indicated otherwise.

^{3/} Nicotine sulfate except (N = nicotine, LA = lead arsenate, and DDT).

Table 2.--Continued

Compound	Melon- worm	Southern armyworm	Bean leaf roller	Southern beet webworm	Blister beetle adult	Spider Mites	Macro- siphum ambro- siae
Didodecylnicotinium dioleate		NS					
Didodecylnicotinium dithiocyanate		NS					
Hexadecylnicotinium bromide	NS, DDT	LA	LA	DDT	C	N	N
Hexadecylnicotinium thiocyanate	NS, DDT	LA	LA	DDT	C	N	N
Methylnicotinium stearate	N	N				N	N
p-Nitrobenzylnicotinium bromide	D	LA	LA	DDT	C	N	N
p-Nitrobenzylnicotinium chloride	D	LA	LA	DDT	C	N	N
p-Nitrobenzylnicotinium palmitate	N	N				N	N
p-Nitrobenzylnicotinium thiocyanate	NS	NS				N	N
Octadecylnicotinium acetate	N	N				N	N
Octadecylnicotinium bromide	D	LA	LA		C	N	N
Octadecylnicotinium dodecanoate	N	N				N	N
Octadecylnicotinium thiocyanate	D	LA	LA		C	N	N
Octadecylnicotinium valerate	N	N				N	N
Octadecylnicotinium p-toluenesulfonate	N	N	LA			N	N
Octylnicotinium p-toluenesulfonate	N	N	LA			N	N

1/ Better than standard.